Report for 2004TX149B: Novel Polymeric Water Treatment for In Situ Removal of Organic Contaminants from Water Bodies

- unclassified:
 - O No publication.

Report Follows

Novel Polymeric Water Treatment for in Site Removal of Organic Contaminates from Water Bodies.

Objectives:

The contamination of runoff water with pesticides such as atrazine from agricultural fields can be considerable. This contamination exists both as aqueous and sorbed phases. Sorbed phases are associated with colloids suspended in the water. Temporary detention ponds could be used to collect runoff water. The water in these detention ponds could then be treated to reduce the concentration of the contaminants prior to release into streams. Under this grant we proposed to develop a polymer flocculent which would sequester the widely used herbicide atrazine from the solution as well as flocculate and remove suspended colloids. This process could be used to reduce the amount of atrazine present in contaminated water bodies, which would then be allowed to flow into streams and rivers.

The interaction between a cyclic secondary amine and atrazine (Figure 1) has recently been shown to be a reaction involving nucleophilic aromatic substitution (1). This finding, suggested that a polymer flocculent could be modified by the addition of a cyclic secondary amine to the polymer unit which would function to trap

Figure 1. Nucleophilic aromatic substitution of atrazine with a secondary amine.

atrazine onto the polymer. Specifically, Poly(allylamine), an off the shelf polymer flocculent, will be modified with Isonipecotic acid (INP) as shown in Figure 2. This new polymer would allow for the irreversible binding of atrazine to the polymer which would then function to flocculate the suspended clay as well as remove atrazine from contaminated water.

One problem which exists with modifying a polymer flocculent is that the more active sites on the polymer which are modified, the less likely it will function well as a flocculent. Alternately, the less modified it is, the less atrazine will be sequestered. To this end, several polymers will be developed based on percent modification per mer of the original polymer. For these experiments the percents which will be developed will be: 100, 70, 50, 30, and 10. From these, the optimum percent modification will be determined.

Once the best polymer is determined, the synthesis will be scaled up to provide enough for biodegradation studies. The biodegradation studies will determine if the polymer-atrazine complex will degrade and if it does what byproducts are produced.

Progress To Date:

To begin the synthesis, a Di-tert-butyl dicarbonate (BOC) protected form of INP was created following the procedure discussed by Alexopoulos (2) and shown in Figure 2. This was made to prevent the coupled acid from reacting with itself. The next step was to modify the polymer with the BOC-INP. This was done by allowing the BOC-INP to react with the coupling agent (EDCI) first and then adding the polymer to the reaction

vessel (Figure 2). The following step was to remove the BOC group using 3 M HCL to hydrolyze the BOC to but anol which was removed by distillation leaving the polymer-INP in solution (Figure 2).

The first polymer to be made was the 100% modified polymer. This was not soluble in water, which is a requirement for success for these experiments since the contamination is in an aqueous environment. The next polymer that was made was the 30% modified polymer. This polymer is water soluble but has not been tested for flocculation or atrazine sequestration.

Future Experiments:

In the next quarter the 10, 50, and 70 percent modified polymers will be made and characterized. For the rest of the year these polymers will be tested for flocculation and atrazine sequestration. The polymer that shows the most atrazine sequestered while still maintaining flocculation ability will then be tested for biodegradation. The biodegradation studies will show both possibly toxic byproducts from the polymer as well as byproducts from atrazine degradation.

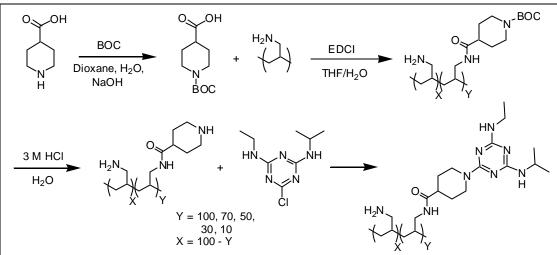


Figure 2. Synthetic procedure for development of the bifunctional polymer.

References

Acosta, E J; Steffensen, M B; Tichy, S E; Simanek, E E, "Removal of Atrazine from Water Using Covalent Sequestration" *Journal of agricultural and food chemistry*. 52, 545 (2004).

Alexopoulos K, Panagiotopoulos D, Mavromoustakos T, Fatseas P, Paredes-Carbajal M. C, Mascher D, Mihailescu S, and Matsoukas J, "Design, Synthesis, and Modeling of Novel Cyclic Thrombin Receptor-Derived Peptide Analogues of the Ser⁴²-Phe-Leu-Leu-Arg⁴⁶ Motif Sequence with Fixed Conformations of Pharmacophoric Groups: Importance of a Phe/Arg/NH₂ Cluster for Receptor Activation and Implications in the Design of Nonpeptide Thrombin Receptor Mimetics" *J. Med. Chem.* 41 328 – 339 (2001).